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STATUS REPORT 8

NASA R-135

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ADVANCED PROJECTS BRANCH

CLOTHING & ORGANIC MATERIALS DIVISION

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Natick, Massachusetts

SUBMITTED BY:

Nathaniel S. Schneider
NATHANIEL S. SCHNEIDER (DR.)
Head, Polymer Chemistry Group

Stuart B. Clough
STUART B. CLOUGH (DR.)
Research Chemist

APPROVED BY:

LEO A. SPANO, Chief, Advanced Projs Br,
Clothing & Organic Materials Division

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INTRODUCTION

This report summarizes some of the results obtained during the initial stages of work on the structure and properties of rubbery polyurethanes. This work was undertaken, at first, as a limited effort to supply data necessary for interpreting the results being obtained on the permeability behavior of structurally controlled samples. However, it was realized subsequently that there were certain unresolved questions concerning the structural organization of the polyurethanes which were important to an understanding of the mechanical as well as the permeability behavior and the scope of the effort was expanded accordingly. This report has been organized both to summarize data on characteristic parameters that are of general interest and to present some preliminary interpretation of the results in terms of polyurethane structure.

A. Transition Temperature Measurements

The determination of transition temperatures in polyurethanes has been carried out primarily in terms of the mechanical test methods (1). Such measurements have identified the presence of two transitions in rubbery polyurethanes; a transition occurring below room temperature associated with vitrification of the sample and a second transition occurring above 100° C where the elevated rubbery plateau modulus undergoes a sharp drop. This behavior is illustrated by modulus temperature

curves for two polyester based samples, taken from work by Cooper and Tobolsky (Fig. 1) (2), which will be discussed more fully later.

Volume-temperature measurements have also been used for determining the low temperature glass transition (3). However, the calorimetric methods have not been used to examine the thermal transitions except in the highest temperature region where a study of decomposition behavior has been carried out by combined differential thermal analysis (DTA) and thermogravimetric analysis (TGA) (4). Perhaps the use of the calorimetric methods to explore a wider temperature range of behavior in the polyurethanes has been discouraged by the reported absence of any discernible low temperature glass transition using DTA (5).

The limitation of DTA was also noted in some early runs on a polyester based polyurethane in the current work. Therefore, the penetrometer or thermomechanical analyzer (TMA) has been used to explore transitional behavior at low temperatures and the differential scanning calorimeter has been used at room temperature and above. The combined results have proven to be especially useful in defining the various mechanical and associated thermal transitions that can be found in the polyurethanes.

(1) Samples

A series of structually controlled laboratory grade samples were supplied by the Mobay Chemical Company. The composition of these samples was 3.2 moles MDI, 2 moles of 1,4 butanediol and 1 mole of prepolymer of molecular weight 2000 whether polyester or polyether. The polybutylene adipate (PBA), polytetramethylene oxide (PTMO), polypropylene oxide (PPO) and polyethylene oxide (PEO) based polyurethanes were all supplied as

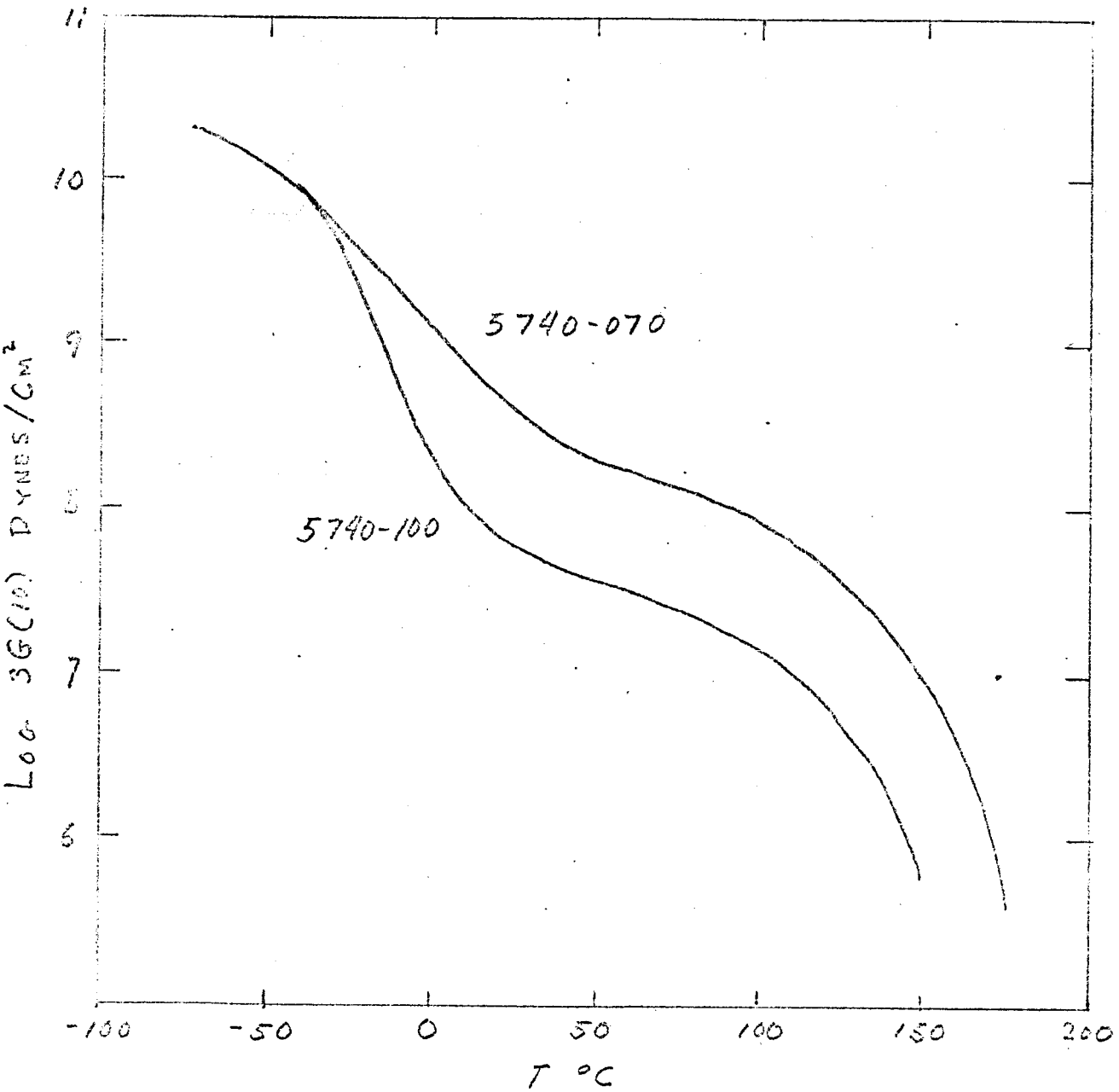


Figure 1. Modulus - temperature curves for two estane polyester type polyurethanes (2).

cured 50 to 70 mil sheet. In addition a semicured 30 mil and a "green" completely uncured PTMO sample were available.

In support of the work on water vapor permeability thermal transitions were also measured on several commercial samples of incompletely specified composition. The Estane samples 5740-070 and 5740-100 are polyester based elastomers reported to contain 1,4 butanediol, MDI and a low molecular weight polybutyleneadipate, with about 39% MDI in-070 and 32% in-100 (2). These two samples are of particular interest since modulus temperature data has been published (2). The Estane sample 5740-140 and du Pont sample LD-550 are both polyether based elastomers probably containing polytetramethylene oxide. The Estane samples 5740-70 and 5740-140 were provided as chopped material in approximately one eighth - inch cubes and the Estane 5740-100 and the du Pont LD-550 were 6 to 10 mil films.

(2) TMA Measurements

The penetrometer module obtainable as an accessory to the du Pont DTA instrument provides a rapid mechanical test method for determining the location of thermal transitions, including the low temperature transition. Since the displacement of the weighted probe with increasing temperature depends on the opposing effects of volume expansion and the drop in modulus which occurs in a transition region, the location of the transition depends on the sample dimensions, choice of heating rate and on the load of the probe. These several factors were investigated and standard conditions involving sample thickness of 1/16" or greater, a

heating rate of 5° C/min., and 5 to 20 g. probe loadings were used. In general, the runs were repeated from three to five times since there was considerable variability in the location of the transition temperature even though a marked transition was observed in each run.

TABLE I

TRANSITION TEMPERATURES OF VARIOUS POLYURETHANES (PENETROMETER DETERMINATION)

SAMPLE	T_1, °C	90% CONF., °C	T_2, °C	90% CONF., °C	T_3, °C	T, °C
Polystyrene			91.8	±2.0		
Neoprene	-46.2	±3.4	28	±1.6		
Polyester Based PU:						
Estane 5740-070	-12.8	±1.6	59.7	±2.1	(-)	
Estane 5740-100	-18.0	±2.4	60.2	±2.7	(-)	
Mobay PBA	-45.2	±3.3	46.4	±3.3	(-)	
Polyether Based PU:						
Mobay PEO	-48.5	±2.1	55.4	±6.4	(-)	
Mobay PPO	-49.7	±3.5	65.3	±4.0	(-)	
Mobay PTMO	-85.0	±2.9	56.0	±5.0	153	7.5
du Pont LD-550	-60.0	±2.0		±3.8	120	8
Estane 5740-140	-51.4	±2.0	67.7	±2.1	(-)	

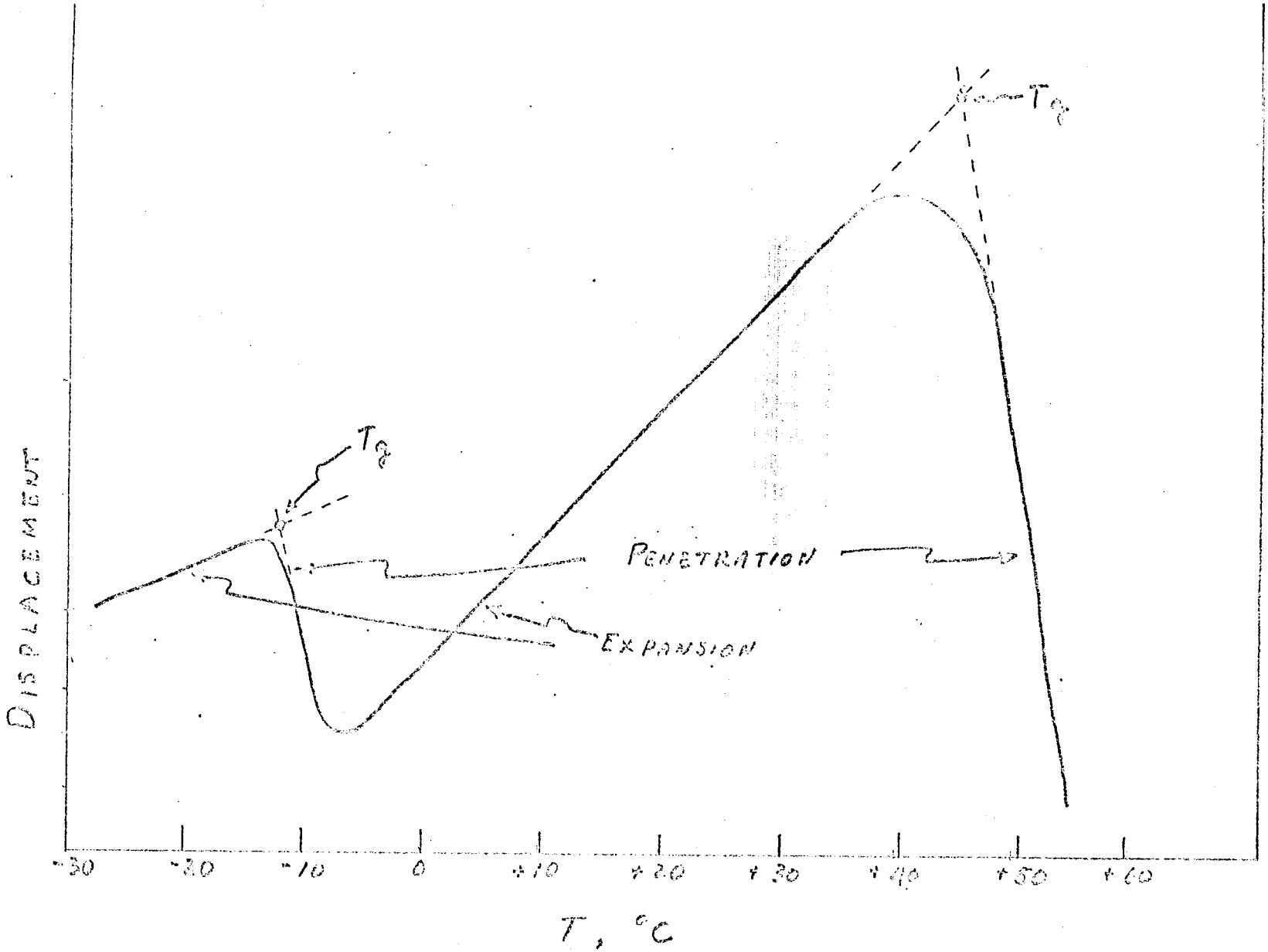


Figure 2. Sample displacement temperature curve for polyester polyurethane obtained with thermomechanical analyzer.

A representative temperature displacement curve for the Mobay PTMO sample is shown in Figure 2, and the results obtained on the various polyurethane samples are tabulated in Table I. It should be mentioned that these samples were not dried prior to the determinations. There is some evidence that in samples saturated with water T_1 is displaced by about 2°C to lower temperatures but T_2 is unaffected.

All of the polyurethanes display at least two transitions, one occurring well below 0°C (T_1) and a second (T_2) in the range 50 to 70°C with the single exception of LD-550. This series of measurements was not extended above 100°C except for two of the samples, LD-550 and Mobay PTMO both of which display a high temperature transition (T_3). Since a transition in this temperature range is commonly observed in the DSC results reported in the section which follows, very likely a transition temperature occurring well above 100° would be found in the other samples as well if the TMA measurements were extended to higher temperatures.

(3) DSC Results

A number of the samples were also run on the Perkin Elmer DSC instrument over the range 40°C to 300°C commonly using scanning rates of 10 deg./min. These samples were first dried 16 hours or longer in a vacuum oven at 50°C and single discs which closely fit the sample cup were cut from the films. Typical scans for the Mobay PTMO and Estane PBA (5740-100) samples appear in Figure 3. The observed transition temperatures are summarized in Table II. An indication of the appearance of the transition is given by numbers next to the transition temperature which correspond to examples sketched below the table. In general the higher the number the more marked the transition.

TABLE II

TRANSITION TEMPERATURES FOR SEVERAL POLYURETHANES
(DSC DETERMINATIONS)

SAMPLE	T_2, °C	T_3, °C	T_4, °C	T, °C
Polyether PU:				
(1) Mobay PTMO 30 Mil Cured Film	82 (3)	152-153 (3)	207-209 (6)	(-)
(2) Mobay PTMO 7-10 Mil Compression Molded, Green Stock	81-83 (3)	162-163 (1)	203-209 (5)	(-)
(3) Mobay PTMO Green Stock	80-83 (1-2)	163-4 (1)	195-200 (5)	(-)
(4) Estane 5740 x 140 Sections From Cubes	90-92 (4)	152-4 (1) (170 2)	203-205 (3-4)	
Polyester PU:				
(1) Mobay PBA 12-15 Mil Film	82 (3)	167 (1-2)	210 (3-4)	
(2) Estane 5740-100 10-12 Mil Film	79 (1)	155-156 (1)		250-260 (1)
(3) Estane 5710 Sections From Cubes	83-86 (1-2)	150-160 (1)		
(4) Estane 5707 Sections From Cubes	86 (2)	(Smeared out Transition Range 125-140°)		200° C (2)

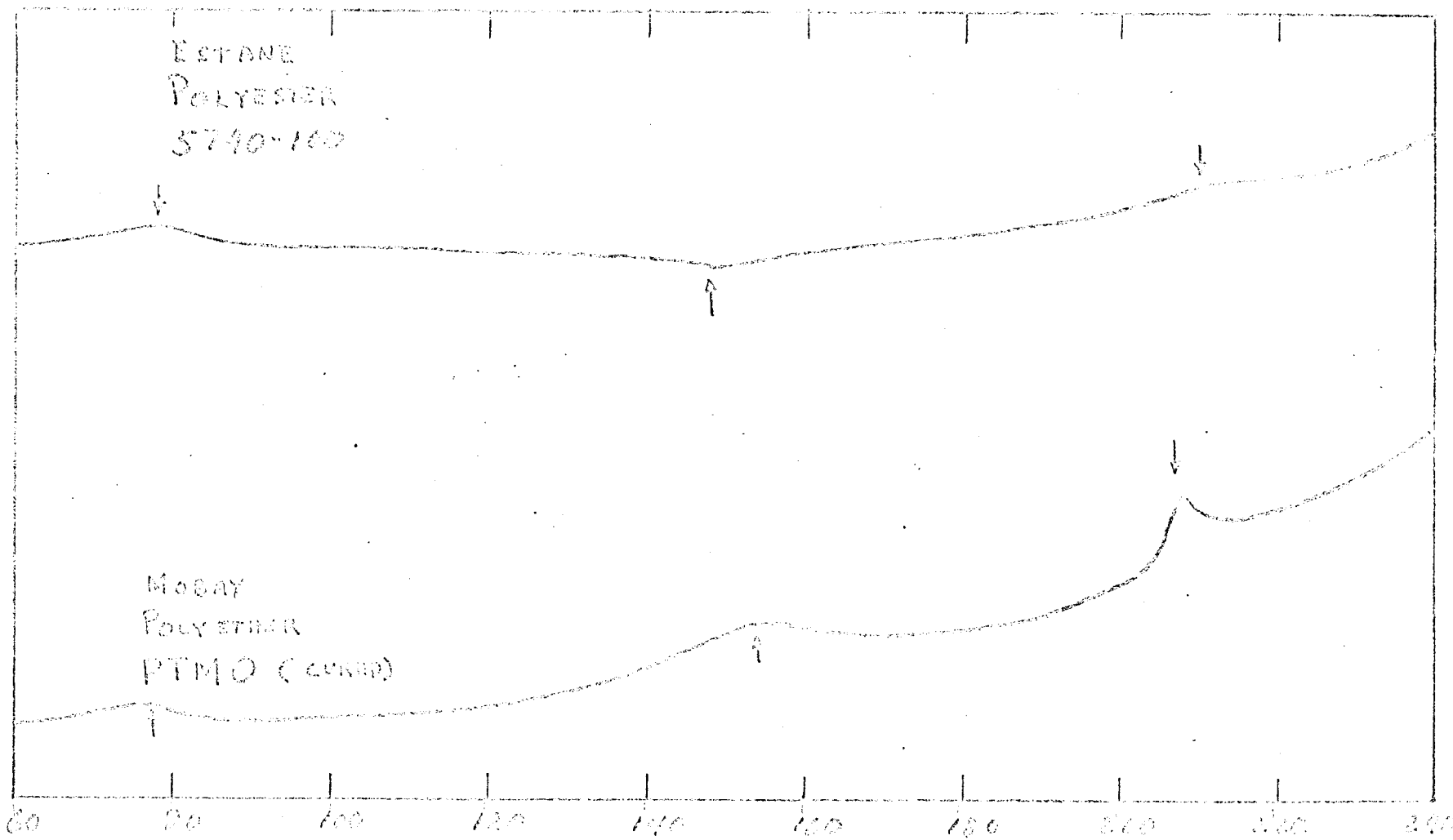
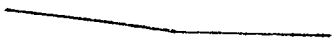
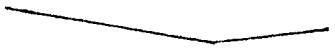
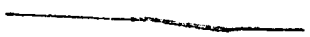


Figure 3. Differential scanning calorimeter traces for a polyester and a polyether type polyurethane.

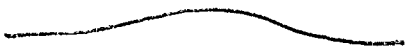
KEY FOR APPEARANCE OF TRANSITION

1)  weak but definite change in slope

2)  sharper change in slope

3)  weak base line displacement

4)  strong base line displacement

5)  weak distributed endothermic

6)  marked endothermic peak

There appear to be three characteristic transitions which occur above room temperature. The 30 mil Mobay PTMO sample displays a pronounced transition at 152-3°C which corresponds precisely with the transition temperature observed by TMA. All of the other samples display a transition (by DSC) in broadly the same temperature range, 140 to 170°C. In addition all of the samples display a transition at 80 to 90°C, and it is tempting to identify these with the T_2 transition revealed at 20°C lower temperatures by the TMA. There are also transitions in almost all samples near or above 200°C. In the Mobay PTMO this appears as a fusion peak rather than a displacement in heat capacity.

In addition there are variable and sometimes highly irregular peaks occurring at still higher temperature, manifestations of sample degredation, most of which are not reported.

B. Optical Analysis of Structure

1. Visual appearance

All of the 50 to 70 mil Mobay polyether based polyurethanes showed turbidity. The PEO was the least turbid, the PPO showed appreciably more turbidity but the 30 mil film and green stock were milky. In contrast the 10-12 mil Mobay PBA sample is clear and even 100 mil thick samples of the Estane 5740-070 and -100 samples were essentially clear. Part of the scattering in the thick sheets was due to surface scattering but even under conditions where this is minimized there is a high level of bulk scattering especially evident in all the Mobay PTMO samples. The turbidity indicates that variations in internal structure are present which give use to fluctuations in refractive index on the scale of the wavelength of visible light.

This turbidity could result from microscopic voids formed perhaps from moisture present during synthesis. The scrupulous attention given to the exclusion of moisture during the synthesis and casting and the clarity of the Mobay PBA film suggest that the turbidity in the polyether sample is not in fact due to microvoids but to inherent structural entities.

2. Optical Microscopy

Polyether samples were compression molded to obtain films of 7-10 mil thickness for examination by polarization optical microscopy. At high magnification (600 x) well separated birefringent spherulitic structure up to 8μ in diameter were observed. The use of a Kofler not stage showed that extinction (between crossed polarizers) of these structures occurred at about 205° C.

3. Light Scattering Measurements

Light scattering measurements were performed on films coated with immersion oil and sandwiched between cover slips to minimize surface scattering. Patterns were photographed using a low intensity gas laser source (632A°) and photometric determinations were made using a Brice Phoenix photometer with suitably narrowed collimating and receiver slits.

Measurements were at first performed on the 30 mil Mobay film and on the 7-10 mil compression molded films but owing to the extremely high level of turbidity in these samples the scattering behavior was dominated by the depolarization arising from secondary scattering. In no case was there any evidence of the typical spherulitic scattering pattern that might have been expected from the microscopically observed birefringent regions.

Reliable measurements were finally carried out on a very thin (1 mil)

solution cast film. This film was free of any evidence of the surface irregularity observed under the microscope in other thin solution cast films. The H_v scattering (measured with polarizer vertical and analyzer horizontal) amounted to about 15% of the V_v scattering (analyzer and polarizer vertical) over the range of scattering angles from 5° to 40°. This indicates that about 20% of the scattering is due to orientation fluctuations and 80% to fluctuations in density. A Fourier inversion of the scattering data revealed that appreciable correlations in density and orientation persist to distances of well over 1 micron. Since the relative orientation and density correlation functions are completely superimposable both types of scattering arise from the same structure. It can also be concluded that the contribution of secondary scattering is negligible. There is evidence that the correlation function can be resolved into two distinct regions and the results will be submitted to further analysis to determine whether such an interpretation is warranted.

4. Strain - Optical Coefficient

The birefringence Δ was determined at 25° C. As a function of strain ϵ at low elongations for the Mobay PTMO and PBA samples. The results are summarized in Table III and compared with reported values for natural rubber and polyethylene.

TABLE III

SUMMARY OF OPTICAL - MECHANICAL DATA

SAMPLE	E (kg/cm^2)	$\Delta/\epsilon \times 10^2$	$\Delta/\sigma \times 10^4$ (cm^2/kg)
Mobay PTMO (1)	95	1.29	1.36
Mobay PBA (1)	157	2.4	1.53
Natural Rubber (2)	$(10)^3$	$(.2)^3$	1.95
Polyethylene (2)	150×10^2	3	0.02

(1) Measured values

(2) Literature values

(3) Depends on degree of crosslinking

It is evident that the strain optical coefficient Δ/ϵ is closer to the value of polyethylene than to that of natural rubber and even higher in the clear polyester than in the turbid polyether sample. This could be intrepreted as indicating that the birefringence in these polyurethane samples arises from the orientation of anisotropic structural entities, as in polyethylene, rather than from molecular chain orientation as in natural rubber.

However, the stress optical coefficients Δ/σ for both polyurethane samples are in the same range as that of natural rubber. The correspondence in Δ/σ, in contrast to Δ/ϵ values, is due to the higher modulus values of the polyurethane samples.

5. X-ray Diffraction

The X-ray diffraction pattern of the unoriented Mobay PBA as well as the PTMO sample showed only an amorphous halo. The polyether at an extension ratio of 4.5 showed a crystalline pattern consisting of three prominent but diffuse equatorial maxima. The weaker layer line spacings present in oriented crystalline polytetra methylene oxide (6) were absent in the oriented polyurethane sample. The polyester sample at an extension ratio of 3 showed two diffuse equatorial maxima and, again, no evidence of layer line spacings. No patterns were taken of samples at any other extensions.

DISCUSSION

The multiple thermal transitions observed in the polyurethanes are evidence of discreet changes in the structural organization and perhaps in molecular structure that occur with increasing temperature. Evidently T_1 is the vitrification temperature or low temperature glass transition that has also been observed by mechanical and volume expansion measurements (1,3). Since T_1 increases with concentration of the aromatic diisocyante (3) it is difficult to make comparisons of these results with others reported in the literature. However, the values for the two polyester based Estane samples compare favorably with values of -10°C for 5740-70 and -23°C for 5740-100 estimated from the modulus temperature curves obtained by Cooper and Tobolsky (2). Furthermore, the trend of T_1 values for the polyethers is consistent with Dickinson's observation that PTMO based samples have the lowest T_g while the T_g values for the other two polyether based samples are similar but substantially higher (7). The relative values of T_g for the three Mobay polyether samples, however, differ from the temperature of the mechanical loss peak at 1 C/S reported as -55°C for PEO, -60°C for PPO and -74°C for PTMO, all determined on high molecular weight polyether samples (8). The differences are not unidirectional. They might be due to several factors including: (1) the influence of crystallinity on the T_g of the polyethers; (2) the effect of low prepolymer molecular weight on the T_g of PTMO measured by TMA and PPO - determined by extrapolation to zero urethane content (3); (3) influence of the aromatic urethane regions.

The transitions identified by TMA at 50-60°C (T_2) and by DSC at

80-90°C (T_2) and at 140-160°C (T_3) are more difficult to assign. Since there is no transition observable by DSC from 40 to 80°C and correspondingly no transition found by TMA from 60 to 100°C it seems logical to conclude that, in fact, the T_2 transition observed by DSC is the counterpart of the T_2 transition revealed by TMA but shifted -20°C, perhaps as a result of the decline in modulus with temperature which occurs even over the plateau region of the mechanical data. However, even with this simplification the problem remains that there is no evidence in the mechanical data for any transition occurring over the temperature range 50-90°C which in fact, corresponds to almost the middle of the rubbery plateau region (2). Further evidence on the nature of this transition will be discussed after considering the transition T_3.

On first consideration the assignment of T_3 appears uncomplicated. The sharp decline in the elevated rubbery modulus of the polyurethanes usually occurs in the range of T_3. As an example, Cooper and Tobolsky's data on the Estane samples are consistent with a transition temperature above 120°C while the transition temperatures of the Mobay polyester samples which he studied occur somewhat above 150°C. The nature of this transition remains controversial. The transition has been discussed in terms of a dissociation of the strong secondary bonding forces between aromatic urethane regions of the chain. These interactions are responsible for many of the properties which distinguish polyurethane elastomers from covalently crosslinked rubbers including reversible elasticity in linear and therefore thermoplastic polymers and advantageous mechanical and ultimate properties. The bonding has commonly

been ascribed to pairwise intermolecular hydrogen bonding (9,10). More recently Cooper and Tobolsky have suggested that an association of the soft and hard segments of the polyurethane chains occur in analogy with the behavior of styrene-isoprene block copolymers. In this latter system specific interaction forces are clearly of less importance than the organization of the styrene and isoprene segments into regions large enough to give rise to two distinct glass transitions. It is clear from their model that Cooper and Tobolsky regard T_3 as the glass transition concerned with the aromatic urethane segments.

However, there is evidence that an alternative assignment for T_3 is more appropriate. It has been suggested that T_3 corresponds to the temperature at which allophonate bond dissociation occurs (11). In keeping with this explanation it has been noted that below about 150° C the polymer acts as though it were lightly crosslinked since an irregular extrudate is produced but above 150° C a smooth uniform extrudate is obtained (11). It has also been noted in the current work that this transition is somewhat weaker in the green PTMO stock (see Table II).

If the assignment of T_3 as the temperature of allophonate bond dissociation is correct then T_2 can be identified as the transition which represents the dissociation of a secondary bonded network. This is consistent with the dissociation temperature of low molecular weight urethanes (11). There is still the need to account for the absence of an equally distinct mechanical transition at T_2. Perhaps this is a result of a gradual softening below the transition, as evidenced by the decline of the modulus and, additionally, the persistence of polar interactions

which restrain segmental motion above the transition. Evidently, the relation between the mechanical behavior and thermal transition needs further consideration.

Finally, at 200-210° there is a transition (T_4) especially prominent in the PTMO sample. Although this is approaching the temperature of urethane bond dissociation (4,12) the transition in PTMO is definitely connected with the spherulitic regions which melt out at this temperature. These high melting regions are probably composed of aromatic urethane segments which have crystallized as the results of association either in the intact polymer or following some chain scission under molding conditions. The high temperature appears consistent with the 230°C melting point reported for the urethane formed from m-toluenediisocyanate and hexamethylene glycol (13). It is not expected that there would be any contribution to the X-ray pattern from these regions since the concentration, estimated from the heat of fusion per gram reported for polymers, is only about 1-5%.

The high value of the strain optical coefficient reported in Table III coincides with the high modulus for these elastomers and it appears that this cannot in itself be taken as evidence for domain structure any more than the modulus values. However, if proof of such domain structure can be obtained then the strain optical coefficient in conjunction with bond polarizabilities for the constituent groups might yield some further information about internal organization.

The onset of crystallinity with sample extension indicates that this process must be taken into account in understanding the stress-strain

curve and the ultimate tensile properties for these polyurethanes. Although references have been made to the occurrance of crystallinity in polyurethanes with high molecular weight polyether or polyester segments (14), there does not appear to be any published work dealing with the effect of orientation induced crystallinity on the mechanical properties.

ABSTRACT

This report covers work on the structure of rubbery polyurethanes undertaken in support of water vapor transmission studies. The overall goal is the development of polyurethane films which offer sufficiently high water vapor permeabilities to provide passive thermal control of a space suit by means of pervaporative cooling. Four distinct transition regions common to the different polyurethane samples have been identified in the combined results from a rapid scanning calorimeter and thermomechanical analyzer. The transition (T_1) below $0^{\circ}C$ is the common glass transition. A transition in the region 60-$90^{\circ}C$ (T_2) is tentatively identified with the dissociation of a secondary bonded network formed by interactions between the aromatic urethane segments. The transition at about $150^{\circ}C$ (T_3) is ascribed to allophonate bond dissociation. A final transition at 200-$220^{\circ}C$ could arise from urethane bond dissociation but in at least one type of polyurethane is due to the melting of birefringent regions present in small concentrations. The series of polyether based samples show increasing turbidity from polyethylene oxide to polytetramethylene oxide indicating the presence of regions of structure but there is no X-ray evidence for crystallinity in the unoriented samples. This domain structure, which has been characterized by preliminary low angle light scattering, must play an important role in determining the mechanical and permeability behavior of the polyurethanes. Finally, crystallization occurs on sample extension and undoubtedly governs the stress-strain behavior at higher elongations.

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